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(54) **Alcohol-resistant firefighting foam concentrates**

(57) The invention relates to alcohol-resistant firefighting foam concentrates.

In order to render a synthetic or protein-based foam concentrate, which is ineffective on polar liquid fires, alcohol-resistant in kind, that is to say capable of being employed both on hydrocarbon fires and on polar liquid fires, a polysaccharide is incorporated therein, together with a triblock fluoropolymer consisting of a linear, central portion made up of 5 to 1000 units of at least one polymerized hydrophilic monomer and two identical, hydrophobic and oleophobic ends, each including an end perfluoroalkyl radical.

GB 2 311 219 A

ALCOHOL-RESISTANT FIREFIGHTING FOAM CONCENTRATES

The present invention relates to alcohol-resistant firefighting foam concentrates, that is to say foam concentrates that can be employed both against hydrocarbon fires and against polar liquid fires.

Firefighting foam concentrates are an effective means of fighting against fires of combustible liquids. When used, they are diluted in mains water or seawater, generally in a concentration by volume of 3 % (that is to say 3 volumes of foam concentrate per 97 volumes of water) or 6 % (6 volumes of foam concentrate per 94 volumes of water). Since the quantity of active substances necessary to satisfy the minimum extinguishing performance that is required is identical in both cases of dilution, foam concentrates that can be diluted to 3 % are twice as concentrated as those that can be diluted to 6 %; they enable the users to stock smaller quantities of foam concentrate, to save space and to reduce storage costs.

After dilution of the foam concentrate with water the resulting mixture produces an aqueous foam by incorporation of air and input of mechanical energy by means of a firefighting nozzle. This foam is poured over the fires of combustible liquids and functions by stifling and cooling until extinction is complete.

Synthetic AFFF (Aqueous Film Forming Foam) foam concentrates have been developed for extinguishing

hydrocarbon fires; these are aqueous solutions including, as main ingredients, a mixture of fluorinated surface-active agents, hydrocarbon surface-active agents and foam-stabilizing solvents, generally
5 belonging to the classes of glycols and of glycol ethers. Examples of AFFF foam concentrates are described, for example, in patents US 3 562 156, US 3 772 195, FR 2 347 426 and US 5 085 786.

Fluoroprotein foam concentrates form the
10 other large class of foam concentrates. In this case the foaming base consists of a hydrolysate of animal proteins, to which fluorinated surface-active agents and foam-stabilizing solvents are added. Such foam concentrates are described, for example, in patents
15 GB 1 280 508 and GB 1 368 463.

The foam concentrates described above cannot be used as they are for extinguishing polar liquid fires. In fact, the foam produced from such foam concentrates is destroyed by the dehydrating and
20 solubilizing effect of polar liquids and cannot be employed for fighting such fires. The most widely employed method for fighting fires of polar liquids consists in incorporating a hydrophilic polymer of high molecular weight into either of the two types of foam
25 concentrates described above; a polysaccharide of thixotropic and alcoholophobic nature is generally employed, more particularly xanthan gum. An alcohol-resistant foam concentrate is then obtained, that is to

say one that can be employed both on hydrocarbon fires and on polar liquid fires. When polar liquid fires are being extinguished, the polysaccharide present in the foam precipitates on contact with the polar liquid and forms a protective gelatinous sheet which insulates the foam against the destructive action of the polar liquid. The foam can then spread over the gelatinous sheet and extinguish the fire. Such alcohol-resistant foam concentrates are described in the following patents: US 4 464 267, US 4 149 599, FR 2 206 958 and WO 92/15371.

The extinguishing of polar liquid fires with the aid of an alcohol-resistant foam concentrate is proportionately more efficient the larger the quantity of polysaccharide present in the foam concentrate. On the other hand, however, since polysaccharides in aqueous solution are macromolecules that increase viscosity, they considerably increase the final viscosity of the foam concentrate, and this gives rise to pumpability problems in the injection systems. In these conditions the majority of alcohol-resistant foam concentrates contain the necessary quantity of polysaccharide to be capable of being diluted only to 6 % on polar solvent fires. Since the extinguishing efficiency of these same alcohol-resistant foam concentrates on hydrocarbon fires depends on ingredients other than the polysaccharide, versions that can be diluted to 3 % and others that can be

diluted to 6 % on hydrocarbon fires exist. Alcohol-resistant foam concentrates of the 6x6 type (diluted to 6 % on hydrocarbon fires and to 6 % on polar liquid fires) and of the 3x6 type (diluted to 3 % on hydrocarbon fires and to 6 % on polar liquid fires) are then obtained.

Alcohol-resistant 3x3 foam concentrates (which can be diluted to 3 % both on hydrocarbon fires and on polar liquid fires) have recently been developed. The advantage of these 3x3 foam concentrates in relation to the 6x6 foam concentrates is that only half as much thereof needs to be used for an identical efficiency. When compared with the 3x6 foam concentrates, they offer the advantage of being capable of being stored with a single mixing system whatever the nature of the fires and of thus eliminating the risk of metering error.

The improvement in the extinguishing efficiency on polar liquid fires and, thereby, the development of 3x3 foam concentrates can take place by following two routes.

First of all, it is possible to lower the viscosity of the polysaccharide. Patent EP 595 772 describes the combined use of a polysaccharide with an anionic hydrophilic polymer making it possible to prepare solutions of low viscosity, these solutions forming part of the composition of the alcohol-resistant 3x3 foam concentrates. Patent EP 609 827

describes the combined use of a polysaccharide and of an alginate and indicates that the viscosity of an alcohol-resistant 3x3 foam concentrate can be reduced by controlling the relative proportions of the polysaccharide and of the alginate; the viscosity can also be reduced by controlling the ratio of the concentration of the aryl- or alkylaryl sulphonic acid salts to the concentration of the other hydrocarbon surface-active agents. In patent ES 2 040 176 the polysaccharide is in a form which is dispersed with the aid of hydrophobic colloidal silica and the quantity of water in the foam concentrate is reduced to a minimum, with the result that the polysaccharide, which is soluble only in water, does not increase the final viscosity of the foam concentrate.

Another means of reducing the viscosity consists in decreasing the content of polysaccharide in the foam concentrate. However, in order to maintain the same extinguishing properties of the final foam concentrate, the effectiveness of the polysaccharide must be increased. Patents FR 2 636 334 and 2 637 506 describe the chemical modification of the polysaccharides by grafting perfluoroalkyl groups onto the hydrophilic side chains of the polysaccharide. The presence of perfluoroalkyl radicals increases the alcoholophobic nature of the polysaccharide and improves its effectiveness in forming an insoluble gel at the surface of the polar solvent; this makes it

possible to reduce the polysaccharide content and hence the final viscosity of the foam concentrate. However, this chemical grafting reaction requires heating to 50-70°C for two hours. Patent EP 524 138 relates to alcohol-resistant foam concentrates using a polysaccharide in combination with a fluorinated cotelomer. The fluorinated cotelomer is obtained by radical telomerization of a fluorine-containing telogen with a mixture of unfluorinated acrylic or methacrylic monomers, the telomerization being initiated by a hydrocarbon azo initiator. One of the monomers is a nonionic hydrophilic monomer and the other an anionic hydrophilic monomer. The combined use of such a fluorinated cotelomer with the polysaccharide reinforces its effectiveness and allows smaller quantities to be incorporated and hence less viscous alcohol-resistant foam concentrates to be obtained.

The present invention falls within the context of the combined use of a polysaccharide with a fluorine-containing product with the aim of increasing the extinguishing efficiency on polar solvent fires and, consequently, as indicated above, of preparing alcohol-resistant 3x3 foam concentrates that can be diluted to 3 % both on hydrocarbon fires and on polar liquid fires.

It has now been found that the addition, to the firefighting foam concentrates, of a polysaccharide and of a triblock fluoropolymer including a polymerized

hydrophilic central portion and two identical, hydrophobic and oleophobic, polyfluorinated ends makes it possible to increase their alcoholophobic nature and to make them effective against polar liquid fires;

5 alcohol-resistant foam concentrates can thus be prepared, that is to say ones that can be employed both against hydrocarbon fires and those of polar liquids. The extinguishing efficiency on polar liquid fires of a foam concentrate containing a polysaccharide and a

10 triblock fluoropolymer according to the invention is superior to that of a foam concentrate containing only a thixotropic polymer of the polysaccharide type. By virtue of the triblock fluoropolymer according to the invention it is possible to prepare alcohol-resistant

15 foam concentrates which are more efficient on polar liquid fires at the same polysaccharide content as the conventional alcohol-resistant foam concentrates or else to prepare foam concentrates which are equivalent in efficiency to conventional alcohol-resistant foam

20 concentrates but containing a smaller quantity of polysaccharide, and this results in foam concentrates that are less viscous and easier to pump in injection and dilution systems, above all at low temperature.

According to the invention there is provided

25 an alcohol-resistant firefighting foam concentrate which comprises a polysaccharide and, additionally, a triblock hydrophilic fluoropolymer comprising a linear central portion made up of 5 to 1000 units of at least

one polymerized hydrophilic monomer and of two identical, hydrophobic and oleophobic end portions, each including an end perfluoroalkyl radical.

The triblock fluoropolymers which can be employed in the context of the invention include a polymerized hydrophilic central portion and two identical, hydrophobic and oleophobic polyfluorinated ends. They are prepared by radical polymerization of at least one hydrophilic monomer, the polymerization reaction being initiated by an initiator bearing two perfluoroalkyl groups at its ends.

The polymerization process includes an initiation step during which the decomposition of the initiator produces two primary radicals, each possessing an end perfluoroalkyl group; these radicals next react, during the propagation step, with the hydrophilic monomer(s) to produce radical oligomers or macro-radicals which have a perfluoroalkylated end. The termination step takes place either by disproportionation between two radicals resulting in two diblock polymers, each made up of a polymerized portion and of a single perfluoroalkylated group, or by recombination of two macroradicals, resulting in a single triblock polymer made up of a polymerized hydrophilic central portion and of two identical perfluorinated ends, or, alternatively, by recombination of a growing macroradical with a primary radical originating from the decomposition of the initiator, also resulting in a

triblock polymer.

In order to obtain triblock flucropolymers according to the invention it is preferable to employ a large quantity of initiator, greater than 1 mol% relative to the monomer(s) and/or to choose hydrophilic monomers which, in the polymerization process, result predominantly in termination by recombination. Acrylamide and its derivatives and acrylic acid and its salts and its esters can be employed alone within the scope of the invention. In the case of a monomer which, for example like methacrylic acid, disproportionates to a high degree, it is preferable to perform the polymerization of this monomer with a comonomer which recombines, like, for example, acrylic acid. In this case the cross-termination promotes the recombination and completely overshadows the disproportionation.

Examples which may be mentioned of hydrophilic monomers that can be employed are:

- acrylic acid and its alkali metal or quaternary ammonium ion salts,
- acrylates of aminoalcohols such as 2-dimethylaminoethanol, 2-diethylaminoethanol and 2-morpholinoethanol,
- acrylamide and its derivatives such as 2-acrylamido-2-methylpropanesulphonic acid, N-methylacrylamide, N-ethylacrylamide, N,N-dimethylacrylamide, N,N-diethylacrylamide, N-methyl-N-ethylacrylamide, N-hydroxymethylacrylamide,

N-(3-hydroxypropyl)acrylamide and N-(2-hydroxyethyl)-acrylamide;

- N-vinyl-2-pyrrolidone and its derivatives such as N-vinyl-3-methyl-2-pyrrolidone, N-vinyl-4-methyl-2-pyrrolidone and N-vinyl-5-methyl-2-pyrrolidone,

- vinyl acetate, polymerization then being followed by hydrolysis to convert the resultant hydrophobic polyvinyl acetate into hydrophilic polyvinyl alcohol.

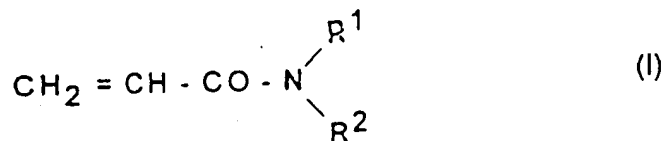
Some monomers described above, in particular the aminoalcohol acrylates, can be cationized before or after polymerization with the aid of an acid like hydrochloric acid, methanesulphonic acid or acetic acid, in order to increase their hydrophilic nature.

A single hydrophilic monomer or a mixture of hydrophilic monomers may be employed.

Methacrylic monomers like methacrylic acid, its salts and its esters give rise to a large extent to terminations by disproportionation. If it is desired to employ such a monomer, it is preferable to employ it as a mixture with a monomer resulting in a termination by recombination, such as those described above.

Among the abovementioned hydrophilic monomers, those preferably chosen will be:

a) acrylamide and its derivatives corresponding to the formula:



in which each of R^1 and R^2 , which may be the same or different, represents a hydrogen atom or an alkyl or hydroxyalkyl radical containing 1 to 3 carbon atoms;

b) acrylic acid and its alkali metal or
 5 quaternary ammonium ion salts;

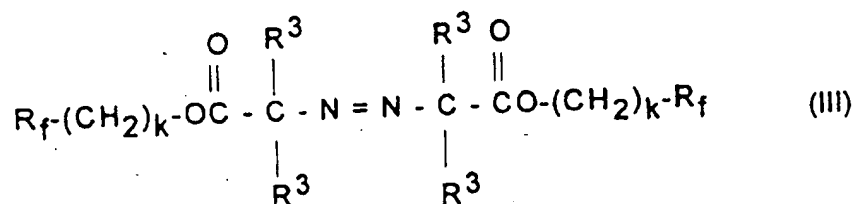
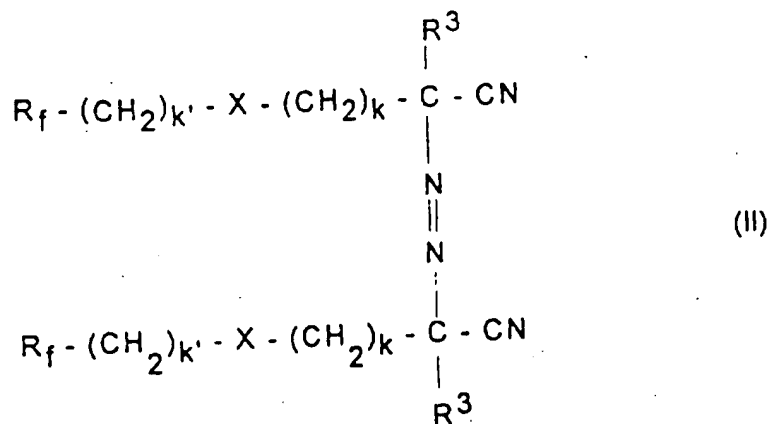
c) vinyl acetate, polymerized hydrophobic polyvinyl acetate portion being subsequently hydrolysed to hydrophilic polyvinyl alcohol.

Acrylamide and/or acrylic acid and its salts
 10 are more particularly employed.

The length of the hydrophilic chain of the polymer, that is to say the number of units of hydrophilic monomer(s), must be 5 to 1000, preferably 10 to 500, and more particularly 20 to 150.

15 The fluorinated initiator is advantageously chosen from perfluoroalkyl azo compounds and perfluoroalkyl peresters.

The perfluoroalkyl azo initiators that can be employed may be chosen from the derivatives
 20 corresponding to the following two general formulae:

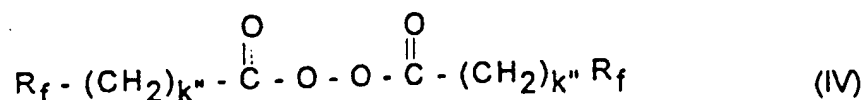


in which formulae R_f is a linear or branched
 perfluoroalkyl radical containing 4 to 20 carbon atoms,
 preferably at least 6; R^3 represents a linear or
 branched alkyl group containing 1 to 4 carbon atoms; X
 5 is a direct bond or an -O-CO-, -CO-O-, -CO-,
 -OCH₂CH(OH)- or -O-CO-NH- group; k is an integer of 1 to
 10, preferably 2 to 6; and k' is 0 or an integer of 1
 to 10, preferably 2 to 6; k' being zero only when X is
 a -CO-O- or -CO- group.

10 The preparation of the perfluoroalkyl azo
 initiators is described in the following publications:
 O. Loubet, University of Montpellier II doctorate
 thesis, July 1991; J.M. Bessiere, B. Boutevin,
 O. Loubet - Polymer Bulletin, 30, 545-549 (1993);

J.M. Bessiere, B. Boutevin, O. Loubet - *Polymer Bulletin*, 31 (6), 673-677 (1993); J.M. Bessiere, B. Boutevin, O. Loubet - *European Polymer Journal*, 31 (6), 573-580 (1995).

- 5 The perfluoroalkyl perester initiators which can be employed may be chosen from the derivatives corresponding to the following general formula:

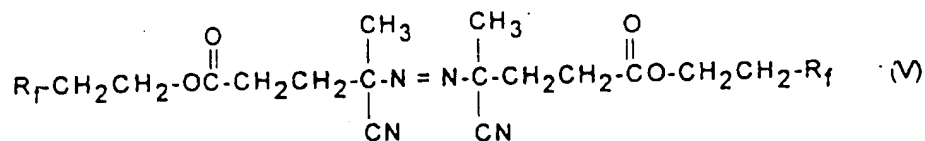


in which R_f has the same meaning as in formulae (II) and (III) and k'' is a number from 0 to 10, preferably 0 to

10 6.

- The preparation and the use of the perfluoroalkyl perester initiators is described in patents EP 405 396, JP 5 097797 and JP 5 170 731 and in the following publications: H. Sawada - Review on
15 *Heteroatom Chemistry*, 8, 205-231 (1993); H. Sawada - *Journal of Fluorine Chemistry*, 61, 253-272 (1993); H. Sawada, Y. Minoshima, T. Hiromitsu - *Journal of Fluorine Chemistry*, 65 (1-2), 169-173 (1993); H. Sawada, K.I. Tamba, M. Oue - *Polymers*, volume 35
20 (18), 4028-4030 (1994).

 Among the initiators that can be employed those chosen will be more particularly the perfluoroalkyl azo compounds corresponding to the following general formula:



in which R_f is a linear or branched perfluoroalkyl radical containing at least 5 carbon atoms.

In order to prepare the triblock fluoropolymers according to the invention a quantity of perfluoroalkyl initiator is advantageously employed which is between 0.5 and 10 mol% relative to the hydrophilic monomer(s), preferably between 2 and 8 mol%. The radical polymerization is performed in a manner known per se, in a solvent capable of dissolving both the monomer(s) and the fluorinated initiator. A solvent with a short hydrocarbon chain is preferably employed, like, for example, acetonitrile, methanol, ethanol or isopropanol. The reaction can take place batchwise or in a flow system. Depending on the type of initiator employed and the boiling point of the solvent, the polymerization temperature is between 50 and 100°C, preferably between 70 and 90°C. The polymer obtained may be soluble or insoluble in the reaction solvent. In the case where the polymer is insoluble in the reaction medium the reaction takes place in a precipitating medium; this latter process of preparation, which produces better homogeneity of the chain length in the final product, will be chosen for preference.

Polysaccharides which can be employed within

the scope of the invention are preferably obtained by aerobic fermentation of carbohydrates under the action of bacteria of the genus *Xanthomonas*.

Heteropolysaccharides are described, for example, in patents US 3 020 206, US 3 915 800, US 3 000 790 and US 3 096 293. Among the heteropolysaccharides employed will be preferably those called "xanthan gum", obtained during the fermentation of sugars under the action of the bacterium *Xanthomonas campestris*. Xanthan gum is an anionic heteropolysaccharide bearing carboxylic groups neutralized with sodium, potassium or calcium cations or a quaternary ammonium ion. The commercial products are generally in the form of powders which can be diluted in water with energetic stirring. As nonlimiting examples of commercial products there may be mentioned Kelco K8A13 from Kelco, Rhodopol 23 from Rhône Poulenc or Actigum CX9YL1 from Systems Bio-Industries; the latter is an anionic macromolecule neutralized with the potassium ion, with an average molecular weight of 2.5 million, represented by the following empirical formula: $[C_6H_7O_5K]_n$, corresponding to a succession of deca-saccharide units.

According to the invention a triblock fluoropolymer and a polysaccharide are incorporated into the synthetic or protein-based firefighting foam concentrates in order to reinforce their resistance to polar liquids.

The synthetic firefighting foam concentrates

contain one or more anionic, nonionic or amphoteric unfluorinated surfactants as foaming base. In the case of the AFFF foam concentrates, the latter additionally contain one or more fluorinated surface-active agents of film-forming nature, capable of greatly decreasing the surface tension; anionic, cationic or amphoteric fluorinated surface-active agents are generally employed.

The protein-based firefighting foam concentrates contain, as foaming base, a hydrolysate of animal proteins which is obtained by basic digestion of bovine horn, hair, hoof or haemoglobin residues, followed by neutralization with an acid. As in the case of the synthetic foam concentrates, the addition of one or more fluorinated surfactants of film-forming nature makes it possible to prepare film-forming fluoroprotein foam concentrates called FFFP foam concentrates. The compositions according to the invention can also be employed as additives to the fluoroprotein foam concentrates called FP foam concentrates, containing a protein hydrolysate and a nonionic fluorinated surfactant and not forming a film, the function of which, among others, is to improve the resistance to contamination with hydrocarbons.

The synthetic or protein-based firefighting foam concentrates may also contain a water-miscible organic solvent, generally a glycol or a glycol ether and more particularly a mono- or diethylene (or

propylene) glycol monoalkyl ether. They may optionally contain various other additives such as an antifreeze agent (for example ethylene glycol or propylene glycol), a cosolvent (for example a lower C₁-C₄ alcohol), a corrosion inhibitor, a preserving agent and a pH stabilizer.

Starting with various foam concentrates described above which can be employed only on hydrocarbon fires, the addition of a sufficient quantity of a polysaccharide and of a triblock fluoropolymer according to the invention makes it possible to prepare alcohol-resistant foam concentrates that can be employed both on hydrocarbon and polar liquid fires. When referred to the total weight of the foam concentrate, the proportion of polysaccharide can range from 0.2 to 5 % (preferably 0.4 to 3 %) and that of the triblock fluoropolymer may range from 0.1 to 5 % (preferably 0.3 to 2 %).

A synthetic foam concentrate of the 3x3 type according to the invention therefore includes, by weight:

- from 1 to 10 % (preferably from 2 to 5 %) of at least one hydrocarbon surface-active agent,
- from 0.5 to 5 % (preferably from 1 to 3 %) of at least one fluorinated surface-active agent,
- from 5 to 30 % (preferably from 10 to 20 %) of at least one water-miscible organic solvent,
- from 0.2 to 5 % (preferably 0.4 to 3 %) of

polysaccharide,

- from 0.1 to 5 % (preferably 0.3 to 2 %) of triblock fluoropolymer, and
- water as complement to 100 %.

5 For the preparation of a synthetic AFFF foam concentrate a film-forming fluorinated surface-active agent is employed, that is to say a fluorinated surface-active agent an aqueous solution of which in a concentration of 1 g/l has a surface tension at 20°C which is lower than 20 mN/m, preferably lower than 10 17 mN/m.

For the preparation of the protein-based foam concentrate of the 3x3 type according to the invention, the starting point is a protein hydrolysate the solids 15 content of which is usually from approximately 20 to 50 % by weight, and to which are added:

- from 5 to 30 % (preferably from 10 to 20 %) of at least one water-miscible organic solvent,
- from 0.2 to 5 % (preferably 0.4 to 3 %) of 20 polysaccharide, and
- from 0.1 to 5 % (preferably 0.3 to 2 %) of triblock fluoropolymer.

To a protein-based emulsion as described above may be added:

- 25
- up to 1 % (preferably up to 0.5 %) of a generally nonionic fluorinated surface-active agent, to obtain an FP fluoroprotein foam concentrate, or
 - from 0.5 to 5 % (preferably from 1 to 3 %)

of at least one film-forming fluorinated surface-active agent, to obtain a fluoroprotein FFFP foam concentrate.

In the examples which follow and which illustrate the invention without limiting it, the efficiency of the firefighting foam concentrates is demonstrated by the following tests:

Sealing and strength of the foam on polar liquid

An automatic balance connected to a recorder is arranged. 50 ml of polar solvent (acetone) are poured into a crystallizing dish placed on the balance pan. Separately, the foam concentrate is diluted to 3 % in mains water and the foam is produced with the aid of an electric whisk for 90 seconds. Approximately 18 g of foam are deposited onto the polar solvent. The balance is reset to zero and the loss in weight, due to the evaporation of the polar liquid, is observed as a function of time. The results are expressed in mg/min. The foam concentrates with the best performance in giving a foam which is leakproof to the vapour of polar liquid are those whose evaporation in mg/min is the lowest. The foam concentrates according to the invention exhibit an evaporation rate lower than 80 mg/min in this test.

During the test the time for total disappearance of the foam on the polar liquid is also determined. The longer this time of disappearance, the better the performance of the foam concentrates. The

foam concentrates according to the invention exhibit a foam disappearance time which is longer than 100 seconds.

Tests are also carried out in more severe conditions on polar liquid fires. In this case the procedure is identical but the polar liquid is ignited and is allowed to burn for 90 seconds before the foam is poured in order to extinguish it. The quantity of polar liquid which is employed is 150 ml and approximately 50 g of foam are poured. In this test the foam concentrates according to the invention exhibit an evaporation rate lower than 160 mg/min.

Similarly, the time for disappearance of the foam on the polar liquid is determined. The longer this time for disappearance, the better the performance of the foam concentrates. The foam concentrates according to the invention exhibit a foam disappearance time of more than 200 seconds.

Expansion

The expansion (or expansion ratio) is the ratio of the volume of foam produced from an aqueous solution containing 3 % of foam concentrate to the initial liquid volume. To determine the expansion 100 ml of aqueous solution containing 3 % of foam concentrate are introduced into a 1-litre test tube and then the solution is beaten for one minute at a rate of one beat per second with the aid of a perforated circular plunger (30 holes of 5-mm diameter,

representing 25 % of the surface) and attached in its centre to a metal rod.

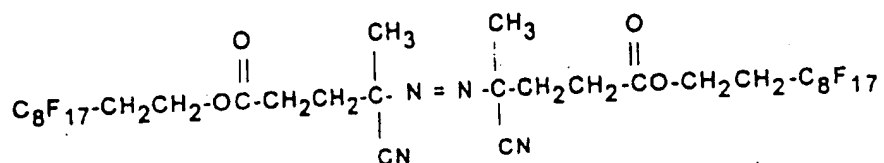
Test for spreading on hydrocarbon

This test, which indicates the rate of formation of the aqueous film on the surface of hydrocarbons, is carried out by pouring 50 ml of hydrocarbon into a Petri dish (diameter: 11.5 cm), the outer face of which is painted black in order to allow the film to be observed. When the surface of the hydrocarbon is motionless 0.5 ml of an aqueous solution containing 3 % of foam concentrate is deposited with the aid of a micro pipette. The solution must be deposited dropwise starting in the middle and by performing an eccentric movement. The stopwatch is started at the instant of the deposition of the first drop and stopped when the film has covered the whole surface of the hydrocarbon. The time is noted. If total covering is not obtained in less than one minute, the percentage of surface covered after one minute is noted.

EXAMPLE 1: PREPARATION OF A FLUORINATED AZO INITIATOR

11.2 g (0.04 mol) of 4,4'-azobiscyanopentanoic acid, 42.8 g (0.092 mol) of 2-(perfluorooctyl)-ethanol and 250 ml of tetrahydrofuran are introduced into a 1-litre reactor equipped with a stirring system, a dropping funnel and a thermometer. 19 g (0.092 mol)

of dicyclohexylcarbodiimide, 0.5 g (0.004 mol) of dimethylaminopyridine and 50 ml of tetrahydrofuran are introduced into the dropping funnel. The stirring speed is set at 700 rev/min and the content of the reactor is cooled to 5°C and then the content of the dropping funnel is added dropwise over 2 hours. After introduction of the content of the dropping funnel the cooling is stopped and the reaction mixture is allowed to return to the ambient temperature (approximately 2 hours). A precipitate is gradually formed and is recovered by filtration. This precipitate, consisting of dicyclohexylurea and of a fraction of the fluorinated azo initiator below:

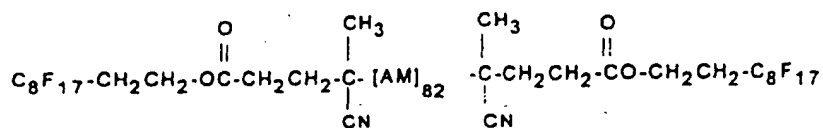


is washed twice with 100 ml of tetrahydrofuran; 8 g of fluorinated initiator are thus recovered. The filtrate is concentrated by evaporation at ambient temperature and methanol is then gradually added to it; this causes the remainder (25 g) of the fluorinated initiator to precipitate. In all, 33 g of fluorinated azo initiator are obtained.

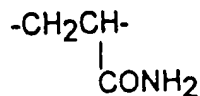
EXAMPLE 2: POLYMERIZATION IN A FLOW SYSTEM

50 ml of acetonitrile are introduced into a 500 ml reactor equipped with a stirring system, a

dropping funnel, a thermometer and a nitrogen entry. A stream of nitrogen is introduced and then, after 30 minutes, the content of the reactor is heated to 80°C. A solution A is prepared separately, containing 5.7 g (0.08 mol) of acrylamide, 6.6 g (0.0056 mol) of the initiator prepared in Example 1 and 150 ml of acetonitrile. 50 ml of solution A are introduced into the reactor and the remainder is placed in the dropping funnel. After 10 minutes' reaction a precipitate appears; the content of the dropping funnel is then introduced gradually over 20 minutes and the reaction continues with a precipitate being formed. After 45 minutes this precipitate is recovered by filtration. The total reaction period, from the introduction of the 50 ml of solution A, is 75 minutes. The precipitate is washed twice with 100 ml of acetonitrile and then dried under vacuum. 5.3 g of a triblock fluoropolymer according to the invention are thus obtained, which has a fluorine content of 9.3 % and the structure of which is the following:

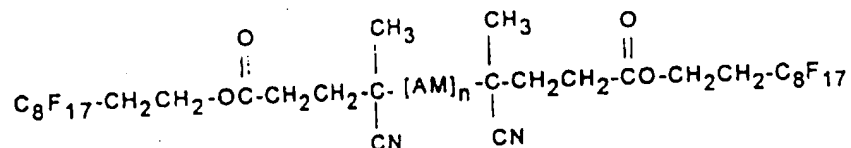


in which AM denotes the divalent group:



EXAMPLES 3 to 6

By operating as in Example 2 a series of fluoropolymers whose chemical structures correspond to the following general formula were prepared:



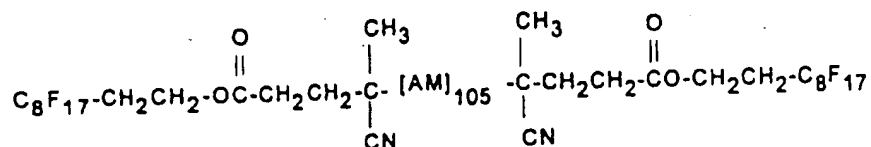
5 The quantity of acetonitrile was kept constant, with 5.7 g (0.08 mol) of acrylamide, and the initiator prepared in Example 1 was employed in quantities corresponding to the fluorine content and to the number of desired acrylamide units. The polymers
10 prepared according to this method are listed in the following table:

Example	Weight of fluorinated initiator introduced (g)	Total reaction period (min)	Fluorine content of the polymer (%)	Value of n
3	0.92	65	3.6	237
4	1.90	45	3.1	277
5	2.81	45	6.1	133
6	4.69	100	7.4	107

EXAMPLE 7: BATCHWISE POLYMERIZATION

200 ml of acetonitrile and 5.7 g (0.08 mol) of acrylamide are introduced into a 500 ml reactor equipped with a stirring system, a thermometer and a nitrogen entry. A stream of nitrogen is introduced and then, after 30 minutes, the content of the reactor is

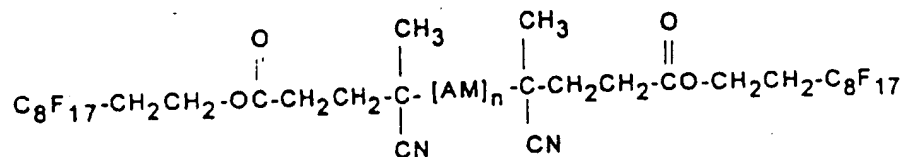
heated to 80°C. 3.8 g (0.0032 mol) of the initiator prepared in Example 1 are poured in rapidly. During the reaction a precipitate forms gradually. 27 minutes after the introduction of the initiator the precipitate is recovered, is washed twice with 100 ml of acetonitrile and is dried under vacuum. A triblock fluoropolymer according to the invention is obtained, which has a fluorine content of 7.5 % and the structure of which is the following:



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EXAMPLES 8 AND 9

By operating as in Example 7 a series of fluoropolymers whose chemical structures correspond to the following general formula were prepared:



The quantity of acetonitrile was kept constant, with 5.7 g (0.08 mol) of acrylamide, and the initiator prepared in Example 1 was employed in quantities corresponding to the fluorine content and to the number of desired acrylamide units. The polymers prepared according to this method are listed in the

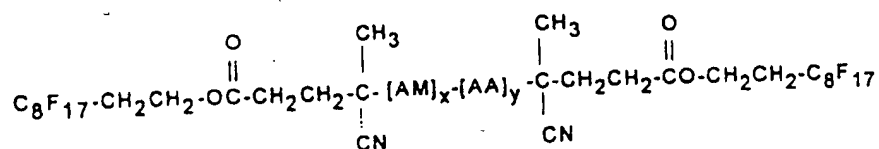
following table:

Example	Weight of fluorinated initiator introduced (g)	Total reaction period (min)	Fluorine content of the polymer (%)	Value of n
8	6.37	90	10.5	71
9	7.78	90	12.5	57

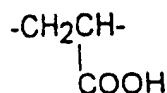
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EXAMPLES 10 to 12

By operating as in Example 7 but replacing the 5.7 g of acrylamide with a mixture composed of 4.6 g (0.065 mol) of acrylamide and of 1.1 g (0.015 mol) of acrylic acid, a series of fluoropolymers were prepared, whose chemical structures correspond to the following general formula:



in which AM has the same meaning as previously and AA denotes the divalent group:



the AM and AA units being distributed randomly.

15

The quantity of acetonitrile was kept constant, with 4.6 g (0.065 mol) of acrylamide and 1.1 g (0.015 mol) of acrylic acid, and the initiator prepared in Example 1 was employed in quantities

corresponding to the fluorine content and to the number of desired acrylamide and acrylic acid units. The polymers prepared according to this method are listed in the following table:

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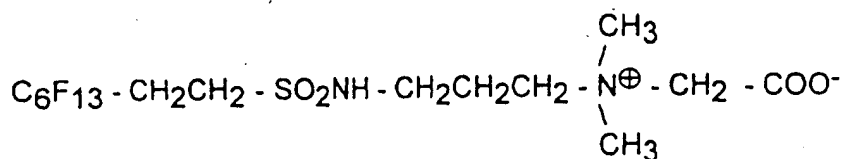
Example	Weight of fluorinated initiator introduced (g)	Total reaction period (min)	Fluorine content of the polymer (%)	Value of x	Value of y
10	2.82	90	5.2	128	30
11	2.05	36	5.0	134	31
12	1.93	40	4.1	167	38

EXAMPLE 13

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To 50 g of an aqueous solution containing 1 % of polysaccharide and prepared by adding to water at ambient temperature some Actigum CX9YL1 polysaccharide from the company System Bio-Industries in the form of powder with energetic stirring, were added, at ambient temperature with moderate stirring, 29.6 g of water, 0.4 g of the fluoropolymer prepared in Example 3, 15 g of butyldiglycol and 5 g of a hydroalcoholic solution containing 27 % of the fluorinated betaine of formula:

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A foam concentrate according to the invention was thus obtained, which was diluted to 3 % with mains water. The resulting solution, subjected to the tests described above, exhibits the following characteristics:

Expansion : 6.0
 Spreading on cyclohexane : 36 seconds
 Sealing on acetone (cold test): 73 mg/min
 Time for disappearance of the foam
 5 on acetone (cold test) : 350 seconds
 Sealing on acetone
 (test on fires) : 159 mg/min
 Time for disappearance of the foam
 on acetone (test on fires) : 600 seconds

10 EXAMPLES 14 to 22

The procedure was as in Example 13 but with
 the 0.4 g of the fluoropolymer of Example 3 replaced
 with 0.4 g of the polymers prepared in Examples 4 to
 12. The foam concentrates thus prepared were diluted to
 15 3 % with mains water and the resulting solutions
 exhibit the characteristics shown in the following
 table:

Example	14	15	16	17	18	19	20	21	22
Fluoro-polymer of Example No.	4	5	6	7	8	9	10	11	12
Expansion	6.0	6.0	5.0	6.0	6.3	6.3	5.0	6.0	6.0
Spreading on cyclo-hexane (seconds)	36	33	35	41	30	52	28	39	26
Sealing on acetone, cold test (mg/min)	72	63	63	72	54	53	63	69	68
Time (s) for disappearance of the foam on acetone (cold test)	>400	>400	>400	>400	>400	>400	>400	370	>400
Sealing on acetone, test on fire (mg/min)	140	133	124	140	103	96	137	148	158
Time (s) for disappearance of the foam on acetone (test on fire)	420	750	>800	690	>800	>800	480	390	450

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EXAMPLE 23: COMPARATIVE

The procedure was as in Example 13 but with the 0.4 g of the fluoropolymer replaced with the equivalent weight of water. A firefighting foam concentrate not in accordance with the invention was obtained, which exhibits the following characteristics:

	Expansion	: 6.0
	Spreading on cyclohexane	: 30 seconds
	Sealing on acetone (cold test):	129 mg/min
10	Time for disappearance of the foam	
	on acetone (cold test)	: 40 seconds
	Sealing on acetone	
	(test on fires)	: 174 mg/min
	Time for disappearance of the foam	
15	on acetone (test on fires)	: 90 seconds

In contrast to the foam concentrates of Examples 13 to 22, containing a composition according to the invention, the foam concentrate containing only the polysaccharide exhibits poor performance on polar liquid, in particular short times for disappearance of the foam on acetone both when cold and on fire.

EXAMPLE 24

By operating as in Example 13 with 0.4 g of the fluoropolymer of Example 2 a firefighting foam concentrate was obtained, a solution of which at a concentration of 3 % in mains water exhibited the

following characteristics:

Expansion : 6.1

Sealing on acetone (cold test): 52 mg/min

Time for disappearance of the foam

5 on acetone (cold test) : >400 seconds

Sealing on acetone

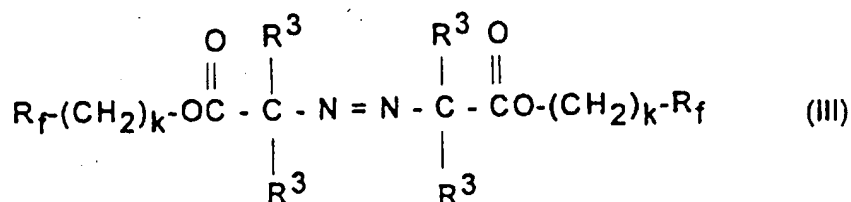
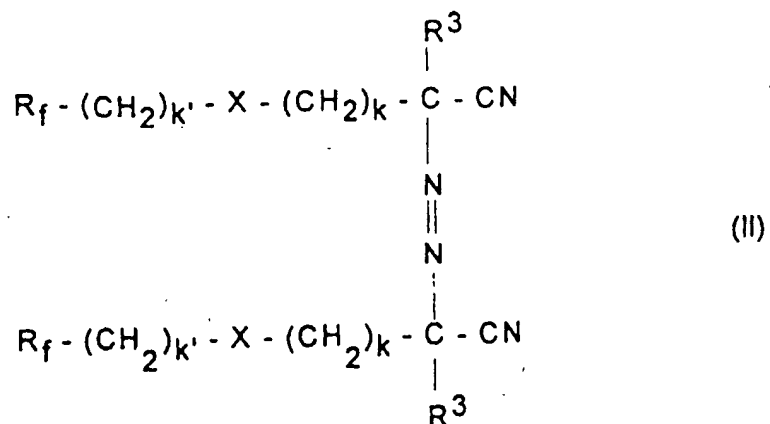
(test on fires) : 97 mg/min

Time for disappearance of the foam

on acetone (test on fires) : >800 seconds

CLAIMS

1. Alcohol-resistant firefighting foam concentrate which comprises a polysaccharide and, additionally, a triblock hydrophilic fluoropolymer comprising a linear central portion made up of 5 to 1000 units of at least one polymerized hydrophilic monomer and of two identical, hydrophobic and oleophobic end portions, each including an end perfluoroalkyl radical.
2. Foam concentrate according to Claim 1, in which the triblock fluoropolymer is obtainable by radical polymerization of at least one hydrophilic monomer, the reaction being initiated by an initiator bearing two perfluoroalkyl radicals.
3. Foam concentrate according to Claim 2, in which the initiator is a compound of general formula II or III:



in which formulae R_f is a linear or branched perfluoroalkyl radical containing 4 to 20 carbon atoms; R^3 represents a linear or branched alkyl group containing 1 to 4 carbon atoms; X is a direct bond or an -O-CO-, -CO-O-, -CO-, -OCH₂CH(OH)- or -O-CO-NH- group; k is an integer of 1 to 10; and k' is 0 or an integer of 1 to 10; k' being zero only when X is a -CO-O- or -CO- group.

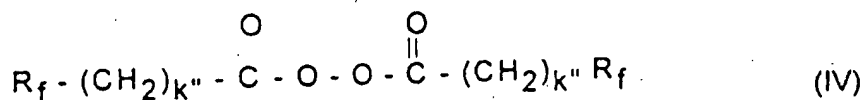
4. Foam concentrate according to Claim 3 in which R_f is a linear or branched perfluoroalkyl radical containing 6 to 20 carbon atoms.

5. Foam concentrate according to Claim 3 or 4 in which k is an integer of 2 to 6 and k' is an integer from 2 to 6.

6. Foam concentrate according to Claim 3 or 4, in which $k=k'=2$ and X is the -O-CO- group.

7. Foam concentrate according to Claim 2, in which the initiator is a perester of general formula

5 IV:



in which k is a number from 0 to 10, and R_f is as defined in Claim 3 or 4.

8. Foam concentrate according to Claim 7 in which k is a number from 0 to 6.

10 9. Foam concentrate according to any one of the preceding Claims, in which the central block of the fluoropolymer includes 10 to 500 units of hydrophilic monomer(s).

15 10. Foam concentrate according to Claim 9 in which the central block of the fluoropolymer includes 20 to 150 units of hydrophilic monomer(s).

11. Foam concentrate according to any one of the preceding Claims, in which the hydrophilic monomer(s) is (are) chosen from:

20 a) acrylamide and its derivatives of general formula:



in which each of R^1 and R^2 , which may be the same or different, represents a hydrogen atom or an alkyl or hydroxyalkyl radical containing 1 to 3 carbon atoms;

- b) acrylic acid and its alkali metal or quaternary ammonium ion salts;
- c) vinyl acetate, polymerization then being followed by hydrolysis to convert the hydrophobic polyvinyl acetate block to a hydrophilic polyvinyl alcohol block.

10 12. Foam concentrate according to Claim 11, in which the hydrophilic monomer is acrylamide, acrylic acid or a mixture thereof.

15 13. Foam concentrate according to any one of the preceding Claims, in which the polysaccharide is a xanthan gum of anionic nature, of average molecular weight greater than or equal to 500,000, in which the carboxylic acid functional groups are neutralized with Na^+ , K^+ or Ca^{2+} cations.

20 14. Foam concentrate according to any one of the preceding Claims, which comprises 0.2 to 5 % by weight of polysaccharide and 0.1 to 5 % by weight of triblock fluoropolymer, the remainder consisting of conventional synthetic foam concentrate ingredients.

25 15. Foam concentrate according to Claim 14 in which the remainder comprises conventional

ingredients of a synthetic aqueous film forming foam concentrate, or a protein-based foam concentrate.

16. Foam concentrate according to Claim 14
in which the remainder comprises conventional
5 ingredients of a fluoroprotein foam concentrate.

17. Foam concentrate according to any one of
the preceding Claims, which has a polysaccharide
content between 0.4 and 3 % and a triblock
fluoropolymer content between 0.3 and 2 %.

10 18. Alcohol-resistant fire fighting foam
concentrate substantially as described in any one of
Examples 13 to 22 and 24.

19. Use of a foam concentrate as claimed in
any one of the preceding claims in controlling
15 hydrocarbon or polar liquid fires.



Application No: GB 9705196.5
Claims searched: all

Examiner: Ian Philpot
Date of search: 4 June 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK CI (Ed.O): A5A (A1)
Int CI (Ed.6): A62D (1/00)
Other: Online WPI (Questel)

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0524138 (Ciba-Geigy) - see whole document	1 at least
X	WO 96/05889 (Dynax) - see page 4 line 12 to page 5 line 9.	1 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.